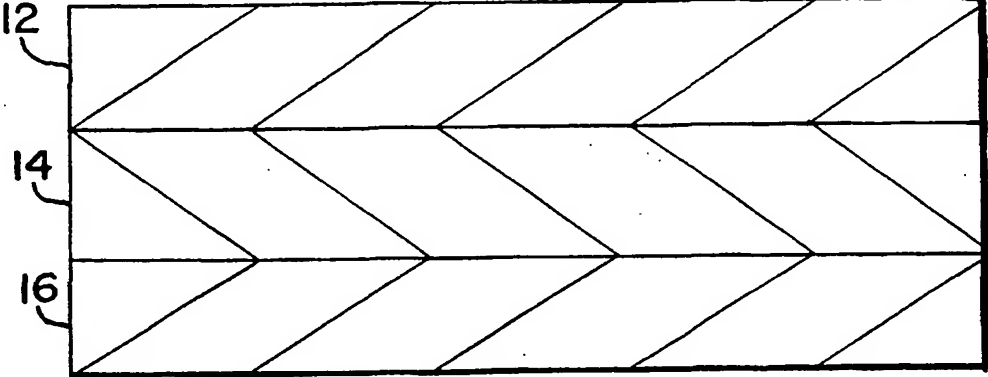


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(21) International Application Number: PCT/US94/07059 (22) International Filing Date: 22 June 1994 (22.06.94) (30) Priority Data: 08/082,226 24 June 1993 (24.06.93) US (71) Applicant: AMERICAN NATIONAL CAN COMPANY [US/US]; 8770 West Bryn Mawr Avenue, Chicago, IL 60631 (US). (72) Inventors: ECKSTEIN, John, P.; 1206 Glenayre Drive, Neenah, WI 54956 (US). ZHENG, Johnny, Q.; 2118 Clover Lane, Appleton, WI 54915 (US). NORDNESS, Mark, E.; 951 Grove Street, Neenah, WI 54956 (US). LIND, Keith, D.; 1806 N. Edgewood, Appleton, WI 54911 (US). WALBRUN, George, H.; 1047 Ida Street, Menasha, WI 54952 (US). SHEPARD, Mary, E.; 1036 Grove Street, Oshkosh, WI 54901 (US). JONES, Gregory, K.; 2653 Sunnyview Road, Appleton, WI 54914 (US). SEEKE, Gregory, J.; 2901 Daniel Court, Oshkosh, WI 54904 (US). (74) Agent: O'ROURKE, Thomas, A.; Wyatt Gerber Burke & Badie, 5th floor, 645 Madison Avenue, New York, NY 10022 (US).		(81) Designated States: AU, CA, JP, NZ, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: IMPROVED STRUCTURES OF POLYMERS MADE FROM SINGLE SITE CATALYSTS		
		
(57) Abstract <p>Copolymers of ethylene and alpha olefins that have been formed by a polymerization reaction in the presence of a single site catalyst, such as a metallocene, are used as a film or as a layer in multiple layer films, including molecularly oriented and irradiated heat shrinkable films (12, 14, 16). Novel blends of the copolymers with other polymeric materials are disclosed and used as a film or a layer in a film particularly in molecularly oriented and heat shrinkable films. Bags made from the multiple layer films are especially useful for shrink packaging primal cuts of meat. Processes for the formation of flexible films and packages made therefrom are also disclosed.</p>		

IMPROVED STRUCTURES OF POLYMERS MADE
FROM SINGLE SITE CATALYSTS

BACKGROUND OF THE INVENTION

Polymeric materials have many applications in packaging structures. They are used as films, sheets, lidstock, pouches, tubes and bags. These polymeric materials may be employed as a single layer or one or more layers in a structure. Unfortunately, there are countless polymeric materials available. Furthermore, resin suppliers frequently have a tendency to claim many more applications for a product than the product is actually suitable for. In addition, in view of the specialized applications and processing problems that are encountered despite the suppliers claims, one skilled in the art can not tell whether a particular resin will be suitable for an application unless tested. However, for various reasons there are frequently drawbacks to the use of many of these polymeric materials. For example, ethylene vinyl alcohol is an excellent oxygen barrier material for use in packaging food products. However, this polymeric material can be affected by moisture that is present in the atmosphere or the packaged product. As a result, it is frequently found that some polymeric materials are better for certain applications than others.

One area where there is a need for suitable resins in film applications is in the area of heat shrinkable films. Heat shrinkable polymeric films are commonly used in packaging meats, particularly primal meat

a hundred pounds or more, along the distribution system.

Because many food products including meat deteriorate in the presence of oxygen and/or water, it is desirable that the bags have a barrier to prevent the infusion of deleterious gases and/or the loss or addition of moisture.

Conventional packaging for many products has frequently been made of multiple layer films having at least three layers. These multiple layer films are usually provided with at least one core layer of either an oxygen barrier material such as a vinylidene chloride copolymer, ethylene vinyl alcohol, a nylon or a metal foil preferably aluminum. Heat shrinkable meat bags, for example, have generally used vinylidene chloride copolymers. The copolymer of the vinylidene chloride may, for example, be a copolymer with vinyl chloride or methyl acrylate. Collapsible dispensing tubes have generally used one or more foil layers. The foil layers in addition to supplying an oxygen barrier also provide the dispensing tube with "deadfold", i.e., the property of a collapsible dispensing tube when squeezed to remain in the squeezed position without bouncing back.

Outer layers of films used in packaging food products can be any suitable polymeric material such as linear low density polyethylene, low density polyethylene, ionomers including sodium and zinc ionomers such ionomers include Surlyn, ethylene vinyl acetate etc. In conventional shrink bags, the outer layers are generally

copolymers formed by a polymerization reaction with a single site catalyst or blends of a polymer and copolymer formed by a polymerization reaction with a single site catalyst and another polymeric material. Examples of suitable polymers for blending include: high and medium density polyethylene (HDPE, MDPE), linear low density polyethylene (LLDPE), low density polyethylene (LDPE), ethylene vinyl acetate (EVA), ultra low density polyethylene (ULDPE or VLDPE), and ionomers such as Surlyn.

The present invention may also be a multilayer structure of at least three layers wherein the core layer is a barrier layer. In one embodiment of the present invention, there may be a first outer layer of an ethylene or propylene polymer or copolymer formed by a polymerization reaction in the presence of a single cell catalyst, a barrier layer and a second outer layer of a polymeric material. The second outer layer may be an ethylene or propylene polymer or copolymer formed by a polymerization reaction in the presence of a single site catalyst or a layer of another polymeric material such as high density polyethylene, medium density polyethylene, linear low density polyethylene, ultra low density polyethylene, low density polyethylene, ethylene vinyl acetate, an ionomer or blends thereof. The first outer layer may also be a blend of the ethylene copolymer with another suitable polymeric material such as described above. A preferred polymer formed by a single site

the metal. These catalysts are frequently used with aluminoxanes as a co-catalyst or an activator, one suitable aluminozane is a methaliumoxane (MAO). Besides, titanium and zirconium, hafnium may also be used as the metal to which the cyclopentadiene is bonded. Alternative metallocenes may include Group IVA, VA and VIA transition metals with two cyclopentadiene rings. Also mono-cyclopentadiene rings or silyl amides may alternatively be in the metallocene instead of two cyclopentadienes. Other metals to which the cyclopentadiene may be attached may include the metals in the lanthanide series. Figures 3, 4, 5 and 6 show representative metallocenes that are suitable single site catalysts.

While the reaction mechanism is not completely understood, it is believed that the metallocene, single site catalyst confines the copolymerization reaction to a single site over the polymer thus controlling comonomer placement and side chain length and branching. The copolymers formed from metallocene single site catalysts are highly stereo regular products with narrow molecular weight distribution. The metallocenes can be used to polymerize ethylene, propylene, ethylenic and acetylenic monomers, dienes and carbon monoxide. Comonomers with ethylene and propylene include styrene, substituted styrene, vinyl, acrylonitrile, methyl acrylate, methyl methacrylate and 1,4 - hexadiene. The metallocene single site catalysts are capable of producing isotactic polymers and syndiotactic polymers, i.e., polymers in which the

A-10⁶ A⁰) from Polymer Labs and a differential refractometer detector. Comparison of the MWD of a 1MI, 0.920 density CGCT polymer with that of 1MI, 0.920 density conventional LLDPE illustrates the very narrow MWD of the CGCT polymers which usually have a M_w/M_n of approximately 2 compared to 3 or greater for LLDPE.

A preferred ethylene copolymer is a copolymer of ethylene and a C₃ to C₂₀ alpha olefin. A preferred copolymer is a low modulus ethylene octene copolymer sold by Dow. This copolymer is formed by Dow's constrained-geometry catalyst technology which uses a single site catalyst such as cyclo-pentadienyl titanium complexes. As best understood, Dow's constrained geometry catalysts are based on group IV transition metals that are covalently bonded to a monocyclopentadienyl group bridged with a heteroatom. The bond angle between the monocyclopentadienyl group, the titanium center and the heteroatom is less than 115°. When the alpha olefin is present in the copolymer in the range of about 10 to 20% by weight these copolymers are referred to as plastomers. When the percent alpha olefin is greater than 20% these copolymers are called elastomers. The preferred ethylene octene copolymer has the octene comonomer present in an amount less than 25%. Examples of the Dow ethylene octene copolymer have the following physical properties.

DENSITY	MOLECULAR	MELT	MELT	
<u>g/cc</u>	MELT <u>WEIGHT DISTRIBUTION</u>	<u>INDEX</u>	<u>FLOW RATIO</u>	<u>STRENGTH</u>
Polymer 1.				
0.920	1.97	1.0	9.5	1.89

of an ethylene, propylene, or styrene polymer or copolymer formed by a polymerization reaction in the presence of a single site catalyst preferably a metallocene. Ethylene may be copolymerized with any suitable monomer such as $C_3 - C_{20}$ alpha olefin including propylene butene-1, 4-methyl pentene-1, hexene-1 and octene-1. A preferred comonomer is octene-1. The preferred ethylene alpha olefin copolymer of the present invention has a density in the range of .880 gm/cc to about .920 gm/cc, a more preferred range of .890 gm/cc to about .915 gm/cc and a most preferred range of about .900 gm/cc to about .912 gm/cc.

Figure 1 shows a cross section of a three layer coextruded structure. Layer 14 is the core layer which may be a barrier layer that minimizes the transmission of oxygen through the structure. Preferred barrier materials are polyvinylidene chloride copolymers such as copolymers of vinylidene chloride and vinyl chloride or an alkyl acrylate such as methyl acrylate. Other preferred barrier material includes, ethylene vinyl alcohol, nylon or a metal foil such as aluminum. Layer 14 may also be a copolymer of ethylene and styrene formed using a single site catalyst in the polymerization reaction. The copolymer of vinylidene chloride may also be polymerized by the polymerization reaction in the presence of a single site catalyst. In addition, layer 14 may also be a polystyrene formed by a polymerization reaction in the presence of a single site catalyst. One such polystyrene is the crystalline syndiotactic polystyrene sold by Idemitsu Petro-Chemical Co., Tokyo, Japan.

In an alternate embodiment of Figure 2, the five layer structure may have a first layer 28 similar in composition to layer 12 of Figure 1, i.e., the film may have a first layer of a polymer formed by the polymerization reaction with a single site catalyst or blends thereof with another suitable polymeric material. One or both of the second 22 and fourth 26 layers may be an adhesive layer.

The composition of adhesive layers 22 and 26 is selected for its capability to bond the core or barrier layer 24 to the surface layers 28 and 30. A variety of the well known extrudable adhesive polymers adhere well to the core or barrier layer 24. Thus, if for example layer 30 is a polypropylene, an adhesive polymer based on polypropylene is desirably selected for layer 26. Examples of such adhesives are the extrudable polymers available under the trade designations Admer QF-500, QF550, or QF-551 from Mitsui Petrochemical Company, or Exxon 5610A2.

If the composition of layer 28 or 30 is an ethylene based polymer or copolymer, an adhesive polymer based on ethylene is preferably selected for layer 22, including ethylene homopolymer and copolymers. Such a preferred adhesive composition is an ethylene vinyl acetate copolymer containing 25% to 30% by weight vinyl acetate. Other ethylene based homopolymer and copolymers, modified to enhance adhesion properties are well known under the trade names of, for example, Bynel and Plexar. Typical base polymers for these extrudable adhesives are the polyethylene and the ethylene vinyl acetate copolymers. Such adhesive polymers, including

Preferred blends using EVA's are those having lower VA content as they tend to yield EVA layers having better hot strength. EVA's having higher VA content tend to yield EVA layers having increased adhesion to for example, the vinylidene chloride copolymer layer. EVA's having virtually any amount of VA will have better adhesion to the vinylidene chloride copolymer layer than an ethylene homopolymer. However, good interlayer adhesion is considered desirable in the invention, and thus, steps are usually taken to enhance adhesion where no unacceptable negative effect is encountered. Thus, higher VA contents, in the range of 6% to 12% vinyl acetate are preferred, a melt index of less than 1 is also preferred. While blend amounts are shown herein in weight percent, VA contents are mole percent. Especially preferred EVA's have VA content of 7% to 9% and melt index of 0.2 to 0.8. Blends of EVA's to make up the EVA component of layers 16 and 18 are acceptable.

The structure of the present invention may be formed by any conventional process. Such processes include extrusion, coextrusion, extrusion coating, extrusion lamination, adhesive lamination and the like, and combinations of processes. The specific process or processes for making a given film which is neither oriented nor cross-linked can be selected with average skill, once the desired structure and compositions have been determined.

When the structure of the present invention is a film, the film may also be oriented either uniaxially or biaxially. Orientation can also be done by any conventional

fabrication processing is a unitary structure.

The second step is orienting the multiple layer film. One method for accomplishing orientation is by heating the film to a temperature appropriate to molecular orientation and molecularly orienting it. The film may then be optionally heat set by holding it at an elevated temperature while its dimensions are maintained. The orientation step is preferentially carried out in line with the first step, which is the film formation step of the process.

The third step is subjecting the formed and oriented multiple layer film, to electron beam irradiation.

The amount of electron beam irradiation is adjusted, depending on the make-up of the specific film to be treated and the end use requirement. While virtually any amount of irradiation will induce some cross-linking, a minimum level of at least 1.0 megarads is usually preferred in order to achieve desired levels of enhancement of the hot strength of the film and to expand the range of temperature at which satisfactory heat seals may be formed. While treatment up to about 50 megarads can be tolerated, there is usually no need to use more than 10 megarads, so this is a preferred upper level of treatment the most preferred dosage being 2 to 5 megarads.

The third step of subjecting the film to electron beam irradiation is performed only after the multiple layer film has been formed, and after molecular orientation, in those embodiments where the film is molecularly oriented. It should be noted that, in the irradiation step, all of the

EXAMPLE 8

LAYER 1 Polyolefin

LAYER 2 Styrene copolymer formed
by the polymerization reaction
with a single site catalyst

LAYER 3 Polyolefin

EXAMPLE 9

Polyolefin

Propylene copolymer
formed by the
Polymerization
reaction with a
single site catalyst
Polyolefin

EXAMPLE 10

LAYER 1 CEO

LAYER 2 CEO

LAYER 3 CEO

EXAMPLE 11

CEO

EVOH

ULDPE-EVA Blend

EXAMPLE 12

CEO-EVA Blend

EVOH

CEO-EVA Blend

EXAMPLE 13

LAYER 1 CEO

LAYER 2 Tie

LAYER 3 PVDC Copolymer
or EVOH

LAYER 4 Tie

LAYER 5 ULDPE-EVA Blend

EXAMPLE 14

CEO

Tie

PVDC Copolymer
or EVOH

Tie

CEO

EXAMPLE 15

CEO-EVA Blend

Tie

PVDC Copolymer
or EVOH

Tie

CEO-EVA Blend

EXAMPLE 16

LAYER 1 EVA-ULDPE

LAYER 2 ULDPE or CEO

LAYER 3 PVDC Copolymer or EVOH

LAYER 4 EVA

LAYER 5 CEO or blend of CEO and EVA

The following examples may also be prepared in
accordance with the present invention:

EXAMPLE 17

Meat Film - Forming Web
Formed by TWQ Process
(Tubular Water Quench Process)

LAYER 1 Nylon

LAYER 2 Tie

coated PET or LDPE.

Example 23

Layer 1 - Blend of two or more copolymers of ethylene and an alpha olefin polymerized in the presence of a single site catalyst or metallocene such as CEO with either CEH or CEB. CEB is a copolymer of ethylene and butene-1 formed by a polymerization reaction in the presence of a single site catalyst or a metallocene.

Example 24

Layer 1- Blend of a copolymer of ethylene and an alpha olefin formed by a polymerization reaction in the presence of a single site catalyst or a metallocene with Polyethylene or other polyolefin such as EVA, EMA, EAA, EMAA, ionomers, ENBA, PP or PPE.

The films of example 23 and 24 can either be single layer films or multi layer films where additional layers are present on layer 1.

13. The film according to claim 8 wherein said alpha olefin is octene-1.
14. The film according to claim 8 wherein said polymeric layer is a blend of said copolymer of ethylene and an alpha olefin with a polyolefin.
15. The film according to claim 14 wherein said polyolefin is a low density polyethylene.
16. The film according to claim 14 wherein said polyolefin is a linear low density polyethylene.
17. The film according to claim 14 wherein said polyolefin is an ethylene vinyl acetate.
18. The film according to claim 14 wherein said polyolefin is a polymer of ethylene and an alpha olefin formed by the polymerization reaction with a single site catalyst.
19. The film according to claim 7-8 and 10-18 wherein said film is molecularly oriented.
20. The film according to claims 7-8 and 10-18 wherein said film is biaxially oriented.
21. The film according to claim 7-8 and 10-18 wherein said film is cross-linked.
22. The film according to claims 7-8 and 10-18 wherein said film is irradiated.
23. The film according to claims 7-8, and 10-18 further comprising a barrier layer.
24. The film according to claim 23 wherein said barrier layer is a copolymer of vinylidene chloride.
25. The film according to claim 23 wherein said barrier layer is ethylene vinyl alcohol.

polymerization reaction with a metallocene catalyst system.

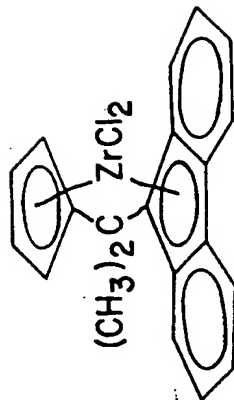
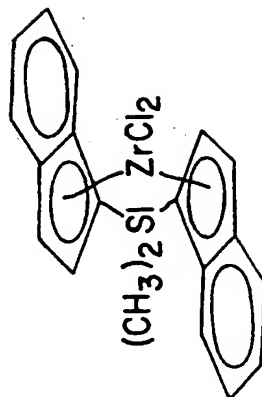
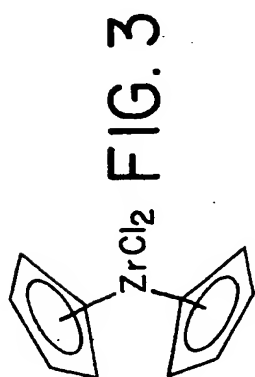
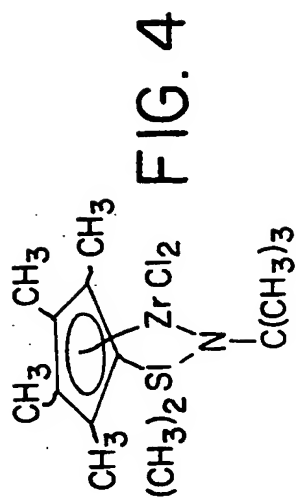
39. The film according to claim 36 wherein said layer comprises vinylidene chloride copolymer formed by the polymerization reaction with a metallocene catalyst system.
40. The film according to claim 36 wherein said layer comprises a polystyrene formed by the polymerization reaction with a metallocene catalyst system.
41. The film of claim 37 where said polymer is a copolymer of ethylene.
42. The film of claim 41 where said polymer is a copolymer of ethylene and a C_3-C_{20} alpha olefin.
43. The film according to claim 42 wherein said alpha olefin is butene-1.
44. The film according to claim 42 wherein said alpha olefin is hexene-1.
45. The film according to claim 42 wherein said alpha olefin is 4-methyl pentene-1.
46. The film according to claim 42 wherein said alpha olefin is octene-1.
47. The film according to claim 42 wherein said polymeric layer is a blend of said copolymer of ethylene and an alpha olefin with a polyolefin.
48. The film according to claim 47 wherein said polyolefin is a low density polyethylene.
49. The film according to claim 47 wherein said polyolefin is a linear low density polyethylene.

with a metallocene catalyst system.

63. The tube according to claim 62 wherein said ethylene polymer is a copolymer of ethylene.
64. The tube according to claim 63 wherein said polymer is a copolymer of ethylene and C_3 - C_{20} alpha olefin.
65. The tube according to claim 64 wherein said alpha olefin is octene-1.
66. The article of claim 35 where said structure is a pouch.
67. The article of claim 35 wherein said structure is a container.
68. The article of claim 1 wherein said layer comprises an amide polymer formed by the polymerization reaction with a single site catalyst.
69. The article claim 35 where said layer comprises an amide polymer formed by the polymerization reaction with a metallocene catalyst system.
70. The article of claims 68 or 69 wherein said amide is a nylon.
71. The film according to claim 2 further comprising a layer of HDPE on said layer of a polymer formed by the polymerization reaction with a single site catalyst.
72. The film according to claim 71 where said polymer is a copolymer of ethylene and an alpha olefin.
73. The film according to claim 72 wherein said alpha olefin is hexene-1.
74. The film according to claim 72 wherein said alpha olefin is octene-1.
75. The film according to claim 73 or 74 wherein said polymer

comprises a layer of an ethylene polymer formed by the polymerization reaction with a metallocene catalyst system.

87. The process according to claims 85 or 86 wherein said film is molecularly oriented.
88. The process according to claim 87 wherein said film is biaxially oriented.
89. The process according to claim 88 wherein said film is irradiated.
90. The process according to claim 87 wherein said polymer is a copolymer of ethylene and an alpha olefin.
91. The film according to claim 24 wherein said film is biaxially oriented and irradiated.
92. The film according to claim 25 wherein said film is biaxially oriented and irradiated.
93. The film according to claim 26 wherein said film is biaxially oriented and irradiated.
94. The film according to claim 57 wherein said film is biaxially oriented and irradiated.
95. The film according to claim 58 wherein said film is biaxially oriented and irradiated.
96. The film according to claim 59 wherein said film is biaxially oriented and irradiated.



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/07059

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☒ Claims Nos.: 19-27 and 52-60
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.